

Spectroscopic and XRD analysis of sulphuric acid treated biodegradable waste

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The number of realized projects in Bulgaria for recovery of poultry wastes as secondary raw material energy resource is limited. However, the problem with recovery of poultry wastes has also no sustainable solution worldwide.

In this paper we investigate the possibility of recovery two types of solid wastes – chicken litter from poultry farm and wood ash from cellulose factory. For the purpose we prepared mixtures of mentioned above wastes and sulfuric acid. The obtained samples were investigated by elemental analysis, powder X-Ray diffraction and Fourier transformed infrared spectroscopy.

It was found that the raw materials have a structure and composition, classifying them as suitable components to obtain soil improvers, due to their content of essential micro-nutrients without excessive of heavy and toxic elements.

Keywords: biodegradable waste, soil improvers, IR, XRD.

INTRODUCTION

It is known that the production of 2000 eggs or the yield of 100 kg of meat is realized the 450–500 kg poultry excrements [1, 2]. In Bulgaria there exist more than 200 poultry farms, growing between 15 and 22 million birds producing daily between 4000–6000 t excrement (chicken litter) and yearly – 500 000 t excrement respectively. The large livestock farms generate a massive soil contamination with excrement residues – nitrates [3, 4]. These environmental damages can be avoided by applying the right techniques and technologies of excrements recovery.

Recently, two chicken litter recovery technologies have been developed through the production of: (i) poultry fertilizers and (ii) biocrackers.

The production of bird fertilizers is suitable technology for removing heavy metals from the soils. The numerous investigations [5–8] proved that suitable combination of inorganic and organic fertiliz-

ers as well as of cultivated vegetation can restore soils contaminated with heavy metals and prevent human health risks by reducing the intake of heavy metals in edible plants [9, 10]. The bird's fertilizers reduce the metal solubility, phytotoxicity and ions exchange. On the other hand, the ash biomass reduces heavy metal concentrations and their ability to penetrate into groundwater. The investigations of biochar are mainly related to energy production, not to soil improvers and fertilizers. In the literature, there is insufficient information on the nutrient properties of biochar. As the biochar is produced by biomass, it is expected to have high carbon content as well as range of macro and micro nutrients for the plants.

In this paper we proposed a new solution for chicken litter application, recovering and additional biomass waste – wood ash to obtain the soil improvers. The selected raw materials and obtained new waste mixtures were examined by elemental analysis, powder X-Ray diffraction and Fourier transformed infrared spectroscopy. It was found that the raw materials have a structure and composition, classifying them as suitable components to obtain soil improvers, due to their content of essential micro-nutrients without excessive of heavy and toxic elements.

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EXPERIMENTAL

Materials

The used raw materials for mixture preparation are: chicken litter (CL), wood ash (WA) and H₂SO₄ (SA). The CL originates in Bulgaria, Kustendil town, “Valentin Georgiev Valdis” company. Approximately 10 kg CL of 28 sampling points were taken. For representativeness of the sample is taken into account the ratio quantity of CL – occupied area of the birds. The WA is a wood burning waste, generated in “Svilosa AD” company, Svishtov town, Bulgaria, where the organized burning of wood generates WA of approximately 10,000 t per year [11]. A quantity of 12 kg WA was taken from 34 sampling points located in the “Svilosa AD” landfill. The representatively of the samples has been achieved by collecting material equal in volume and depth from each sampling point. The used sulfuric acid (Merck) was with a mass percentage (%) concentration in the interval from 10–50%.

The addition of sulfuric acid is a suitable method for elimination of pathogens, molds and fungi in CL [12–13]. The prepared four mixtures of CL + WA + SA (samples S1, S2, S3 and S4) and one mixture of CL + WA (sample S5 – used as control mixture) were dried for 4 h at 60°C. The component mass ratio of the mixtures is shown in Table 1.

Methods

The mixtures were prepared according to EN 14899 “Characterization of waste sampling of waste materials Framework for the preparation and application of a Sampling Plan” and EN 15002 “Characterization of waste. Preparation of test portions from the laboratory sample” as well.

The chemical composition of the raw materials (CL and WA) was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Teledyne Leeman Labs, USA) with dual monitor plasma, “L-PAD” detector (high resolution of 0.007 nm and continuous spectral range from 165 to 1100 nm) and RF generator (power up

to 2 kW at 40.68 MHz). high resolution (0.007 nm), continuous spectral range (from 165 to 1100 nm).

The spectrometer calibrations were made by standard solutions in three concentrations intervals: (i) 0.000–10.000 mg/L; (ii) 0.000–1.000 mg/L; (iii) 0.000–0.100 mg/L. For the zero concentration (0.000 mg/L), the double distilled water was used. As the first concentration interval is very broad, it was necessary to use more than three standard solutions, namely: 1.000, 2.000, 5.000, 8.000 and 10.000 mg/l. The measurements of components with higher concentrations were made after appropriate dissolution, where the obtained results are presented multiplied by dilution factor. At the second and third intervals, three standard solutions are sufficient for calibration: 0.100, 0.500, 1.000 mg/L and 0.010; 0.050; 0.100 mg/L respectively.

Powder X-ray diffraction (XRD) patterns were collected at room temperature in a step-scan regime (a step of 0.05, 2-theta in the range of 5 to 75° 2-theta) on a D2 Phaser – Bruker AXS diffractometer. The experiments were performed in Bragg–Brentano geometry with Ni-filtered K α radiation ($\lambda = 0.15418$ nm) at accelerating voltage of 10 kV and a current of 30 mA.

The measurements of the infrared spectra were performed on a FT-IR Spectrometer Varian 660-IR, Austria, 2009, covering the range of 400–4000 cm⁻¹. The samples have been prepared as pellets consisting of low-dispersed KBr and powder of prepared mixture. The transmittance spectra were collected using MCT detector with 64 scans and 1 cm⁻¹ resolution.

RESULTS AND DISCUSSION

Elemental analysis

The most variable component of CL is the concentrations of nutrients resulting from the processes of aerobic fermentation [14]. These factors affect the chemical composition and properties of the CL, and to the physical qualities [15]. More than 1/3 of the dry matter is determined by the content of

Table 1. Mass ratio of chicken litter, wood ash and sulphuric acid in the mixture samples

No	Mixture sample	Chickenlitter (CL)	Wood ash (WA)	Sulphuricacid (SA)
1.	S5	1.00	1.00	-
2.	S1	1.00	0.10	0.10
3.	S2	1.00	0.50	0.25
4.	S3	1.00	0.75	0.75
5.	S4	1.00	1.00	0.50

microorganisms and germs included in the active biological transformations [16]. Therefore it is very important to make an elemental analysis of essential nutrients to be defined the possibility of subsequent treatment and application [17, 18]. For the purposes we made chemical analysis of micro- and macronutrients and verification for the presence of heavy metals of the raw materials (CL and WA) as well as of the control sample S5.

Table 2 presents the obtained results from the elemental analysis of CL and WA, recalculated as oxides of the relevant elements. The measurements show that the raw materials are suitable for use only as soil improvers, because of the insufficient quantity of the elements. For example, to be classified some material as fertilizer the minimum quantity of $P_2O_5^{tot}$ must be 16%, MgO – 15%, K_2O – 29%, etc. [18], which values significantly exceed those in investigated samples (Table 2). The heavy metals (Cu and Zn) do not exceed the permitted values in EU [19].

Powder X-ray diffraction

Figure 1 shows the XRD patterns of the mixtures. It is seen that the samples have such low intensity of crystallinity. The sample S2 has the

highest degree of crystallinity, where S1 – the lowest one. The phase analysis of S1, S2, S3 and S4 (Table 3) shows relict phases, preserved from the raw materials: quartz (SiO_2) (JCPDS [20] 46-1045: $d, \text{\AA} = 3.34, 4.28$), $CaSO_4 \cdot 2H_2O$ (JCPDS 33-0311: $d, \text{\AA} = 7.63, 4.28, 3.06$), and calcite $CaCO_3$, (JCPDS 24-0027: $d, \text{\AA} = 3.03, 3.35, 1.87$) in all investigated samples as well as new-formed phases as a result of the reaction of CL and WA with SA [21, 22]. The identified new-formed phases are $CaSO_4 \cdot 0.5H_2O$ (JCPDS 41-0224: $d, \text{\AA} = 3.00, 2.80, 6.01$), K_2SO_4 (JCPDS 24-0703: $d, \text{\AA} = 2.90, 2.99, 2.88$), $CaHPO_4 \cdot 2H_2O$ (JCPDS 72-0713: $d, \text{\AA} = 7.59, 4.23, 3.04$), $Ca(H_2PO_4)_2$ (JCPDS 70-1380: $d, \text{\AA} = 3.49, 3.57, 3.63$), $(NH_4)_2SO_4$ (JCPDS 44-1413: $d, \text{\AA} = 4.33, 4.39, 2.65$), KCl (JCPDS 26-0921: $d, \text{\AA} = 3.15, 2.23, 1.82$) and NaCl (JCPDS 26-0920: $d, \text{\AA} = 3.02, 2.23, 1.82$) in S1 and S4 identified in the all SA-treated samples. The formation of $CaSO_4 \cdot 0.5H_2O$ and K_2SO_4 is a result from the reaction of organic sulphur with part of CaO and K_2O , contained in WA, under the impact of acidic reaction medium produced by the mineral acid – H_2SO_4 . The most important from the new-formed phases are $CaHPO_4 \cdot 2H_2O$ and $Ca(H_2PO_4)_2$ (water-soluble salts of Ca and P) [23, 24]. Both are analogues of

Table 2. Chemical analysis of raw materials (CL and WA)

Sample	$P_2O_5^{tot}/\%$	$K_2O/\%$	$Na_2O/\%$	CaO/ %	MgO/ %	Cu/ %	Fe/ %	Zn/ %	B/ %	$SO_3/\%$
CL	3.70 ± 0.06	2.16 ± 0.12	0.31 ± 0.02	10.47 ± 0.72	0.60 ± 0.07	<0.006*	0.12 ± 0.07	<0.03*	<0.010*	0.17 ± 0.01
WA	<0.02*	0.48 ± 0.02	0.40 ± 0.02	3.35 ± 0.17	0.50 ± 0.07	<0.006*	3.20 ± 0.17	<0.03*	<0.010*	0.17 ± 0.01

* The measured concentration is below limit of detection.

Table 3. Identified inorganic phases with powder XRD analysis

Nº	Sample	Identified phases
1	S5	$SiO_2, CaCO_3, CaSO_4 \cdot 2H_2O, Ca_3(PO_4)_2$
2	S1	$SiO_2, CaCO_3, CaSO_4 \cdot 2H_2O,$ new: $CaSO_4 \cdot 0.5H_2O, K_2SO_4, Ca(H_2PO_4)_2, NaCl, (NH_4)_2SO_4$
3	S2	$SiO_2, CaCO_3, CaSO_4 \cdot 2H_2O,$ new: $CaSO_4 \cdot 0.5H_2O, K_2SO_4, KNO_3, KCl, Ca(H_2PO_4)_2, Ca(NO_3)_2, Ca(OH)_2, Mg(OH)_2, (NH_4)_2SO_4$
4	S3	$SiO_2, CaCO_3, CaSO_4 \cdot 2H_2O,$ new: $CaSO_4 \cdot 0.5H_2O, K_2SO_4, KNO_3, KCl, Ca(H_2PO_4)_2, K_2SO_4, Ca(OH)_2, Mg(OH)_2, (NH_4)_2SO_4$
5	S4	$SiO_2, CaCO_3, CaSO_4 \cdot 2H_2O,$ new: $CaSO_4 \cdot 0.5H_2O, Ca(H_2PO_4)_2, K_2SO_4, KNO_3, (NH_4)_2SO_4$
6	CL	$SiO_2, CaCO_3, CaSO_4 \cdot 2H_2O$ [25]
7	WA	$SiO_2, Ca_3(PO_4)_2$ [25]

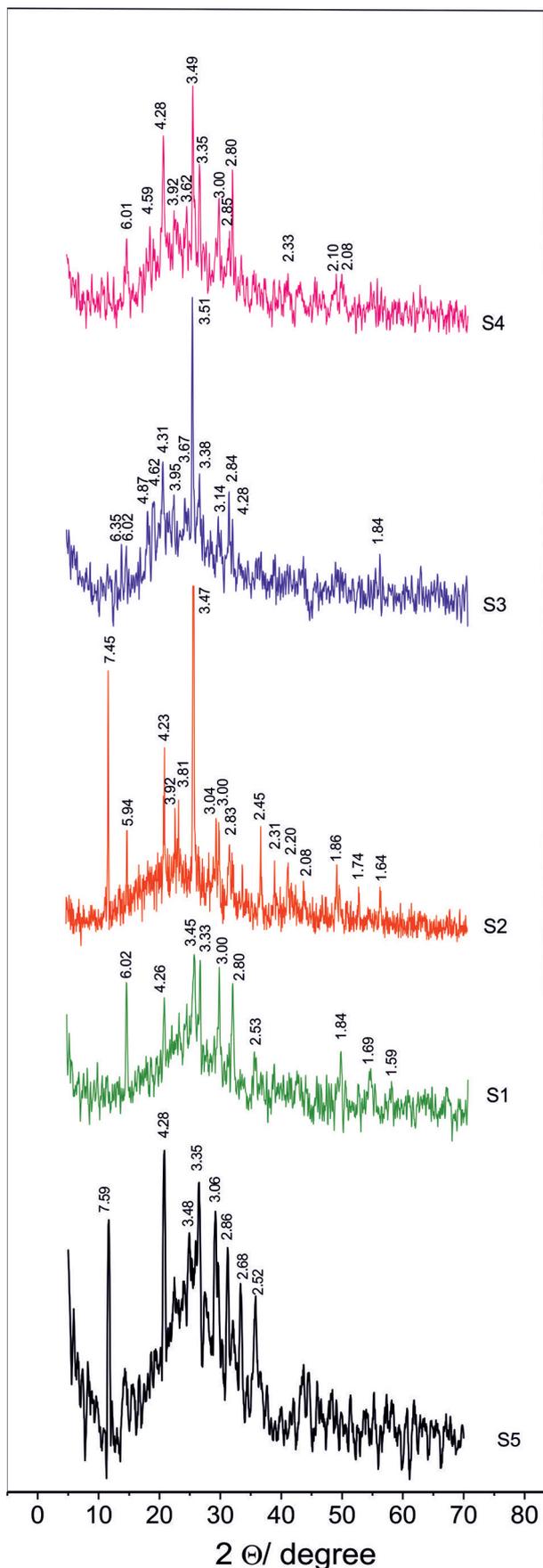


Fig. 1. XRD patterns for mixtures S1–S5.

fertilizer components, because they contained the important for plants Ca, P and H₂O. Also, the formation of gypsum is important as well, as it can be used as improver of acidic soils [21, 22]. Another two new-formed phases: Ca(OH)₂ (JCPDS 44-181: d, Å = 2.62, 4.90, 1.92 and Mg(OH)₂ (JCPDS 44-1482: d, Å = 2.36, 1.79, 4.75) are identified in S2 and S3. Having the highest degree of crystallinity and containing the all identified new-formed phases, the sample S1 shows the most appropriate characteristics for a soil improver.

The organic component and amorphous inorganic salts in the samples was characterized by FT-IR spectroscopy measurements.

Fourier Transformed Infrared Spectroscopy

Figure 2 shows the results from FT-IR measurements of raw CL, WA and selected samples.

The obtained results correspond to a wide variety of functional groups, characterized inorganic and organic components in the investigated samples – methyl and methylene groups, carbonyl, chlorides and sulfonyl chloride, amino groups, hydroxyl groups and carboxyl groups. The presence of inorganic components is considered by bands that can be assigned to the functional groups: carbonate, sulphate and ammonium groups. These bands are situated in several intervals: 1420–1430 cm⁻¹ and 860–780 cm⁻¹ (for carbonates), 1140–1040 cm⁻¹, 615–595 cm⁻¹ (for SO₄) and a wide band ~ 3140–3040 cm⁻¹ which is overlapped with antisymmetric and symmetric stretching vibrations of methyl and methylene groups and also 1397–1398 cm⁻¹ (for NH₄⁺).

The sulphate and carbonate ions are evidence of mineralization process [25, 26]. The presence of the carbonate ion can be explained by the process of mineralization, as well as by inorganic impurities in the raw materials. At the measured spectra are seen and the absorption bands, characteristic for incorporation of P and Si in oxygen compounds [18, 25].

The biggest variety of functional groups of different organic compounds is detected for CL due to incomplete aerobic fermentation processes. In CL-samples the bands of inorganic compounds – sulphates and carbonates have been detected. At WA-sample, the bands of organic components missing and the bands of functional groups of inorganic compounds are identified (mainly quartz and tri-calcium phosphate) only, whose presence is a result from the wood burning. In the spectra of mixtures S1, S3 and S4 was observed the conversion of the methylene groups – “fresh” biomass markers (2923–2929 cm⁻¹) into products of initial mineralization (Fig. 2).

Taking into account the origin of the samples, and the distribution of the absorption bands in the spectra we can made the following findings from FT-IR analysis:

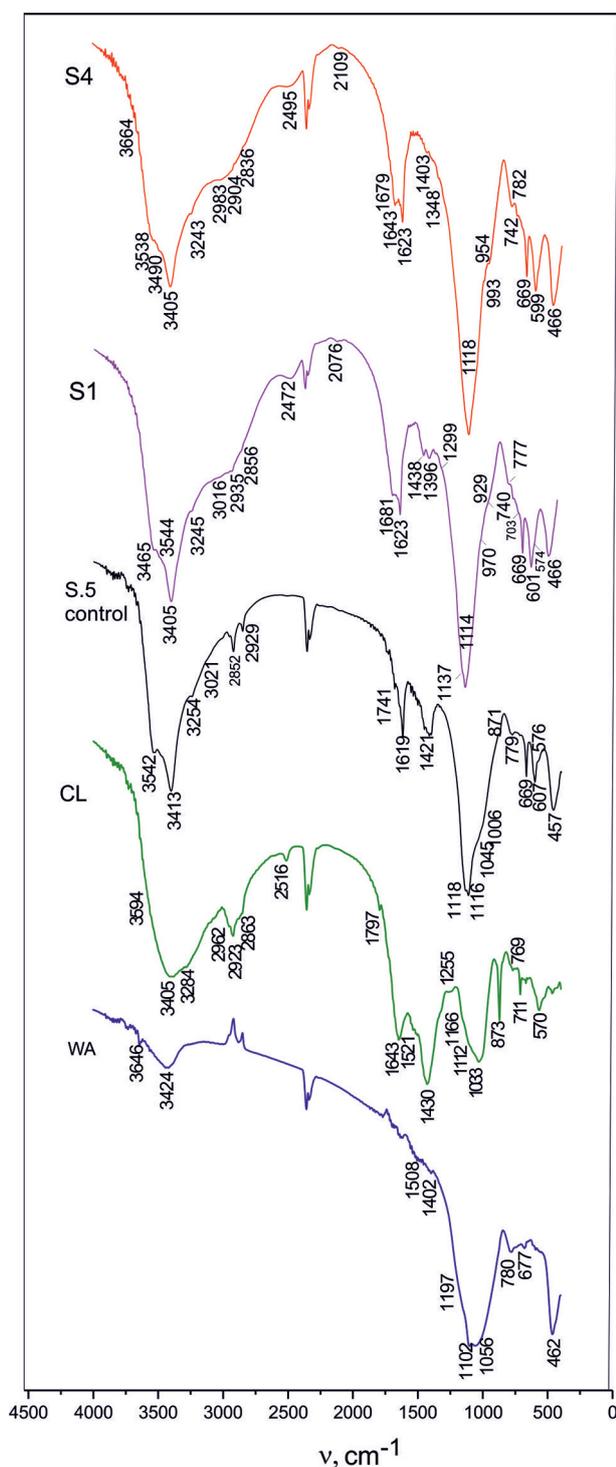


Fig. 2. IR spectrum of mixtures S1, S4, control sample S5 and the raw materials (CL and WA).

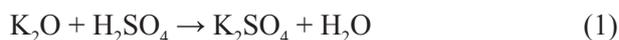
– The absorption bands in 3413–3424 cm^{-1} range are typical for antisymmetric and symmetric stretching vibrations of water molecules. In the spectrum appears a new absorption band at 3540–3550 cm^{-1} [27, 28].

– In the samples CL, S5, S1–S4 there exist fresh – unchanged and non-mineralized part because of: (i) presence of the methylene groups with absorption bands at 2923–2850 cm^{-1} and (ii) presence of C-N groups in primary aromatic amines, detected by oscillation absorption band at 1322 cm^{-1} [27].

– In the samples S1, S3 and S4 start mineralization process, proven by: i) appearance of aliphatic methylene groups bands in the range of 2834–2855 cm^{-1} ; ii) disappearance of the band at 1320–1322 cm^{-1} , and iii) appearance of new bands in the range of 1640–1740 cm^{-1} (observed in the all mixture samples treated with SA). The mineralization process is marked by the transformation of some of the initial organic compounds to new one and the appearance of the functional groups of the inorganic compounds as a result from impact of SA [11–25]. The evidence for the transformation of the methylene groups are the absorption bands of sulphonyl and carbonyl groups to aldehydes, ketones and carboxylic acids and esters.

The FT-IR measurements show that samples S1 are more suitable for soil improver because of established process of mineralization.

The obtaining of required components is possible due to chemical composition of the raw materials and occurs by the following main reactions:



CONCLUSIONS

It was found that the selected raw materials have a structure and composition, which defines them as carriers of essential micro-nutrients for the plants, without excessive content of heavy metals. These findings allow these materials to be classified as suitable for obtaining soil improvers.

The experimental results show that the investigation of the prepared mixture samples with XRD and FT-IR are required to determine the phase composition of inorganic and organic components.

The impact of SA results in acceleration of mineralization process at mixture samples, elimination

of the pathogenic microorganisms in raw materials as well as participation in the synthesis reactions of inorganic compounds.

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